FACTFILE:

GCE CHEMISTRY

5.3 VOLUMETRIC ANALYSIS

Rewarding Learning

Volumetric Analysis

Learning Outcomes

5.3.1 titrate iodine with sodium thiosulfate using starch as an indicator and estimate oxidising agents, for example hydrogen peroxide and iodate(V) ions by their reactions with excess acidic potassium iodide;

5.3.2 titrate acidified potassium manganate(VII) with iron(II) and other reducing agents;

5.3.3 deduce titration equations given the half-equations for the oxidant and the reductant;

5.3.4 understand the method of back titration, for example determine the purity of a Group II metal oxide or carbonate;

Iodine and sodium thiosulfate titration

These titrations can be used to determine the concentration of an oxidising agent. The oxidising agent (e.g. hydrogen peroxide or iodate(V)) reacts, in the presence of acid with an acidified iodide solution and oxidises it to iodine which is 'liberated' in the conical.

When using iodate(V) as oxidising agent, pipette 25.0 cm^3 of standard potassium iodate(V) solution into a conical flask and add 25 cm^3 of sulfuric acid and approximately 1.5 g of solid potassium iodide (excess).

Oxidising agent iodate(V) ions:
$IO_3^- + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2$

When using hydrogen peroxide solution as the oxidising agent, pipette 25.0 cm^3 of hydrogen peroxide solution into a conical flask and add 25 cm^3 of sulfuric acid and excess potassium iodide. The reaction mixture is initially colourless.

Oxidising agent hydrogen peroxide: -
$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$

The iodine produced in the conical (brown solution) is then titrated with sodium thiosulphate solution.

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Ionic equation: $2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$

This titration is carried out by adding standard sodium thiosulfate solution from a burette until the solution in the conical is **straw/yellow** in colour. Starch is then added as indicator and the titration is continued, adding the sodium thiosulfate solution dropwise until the indicator changes colour from **blue-black** to **colourless** at the end point.

Potassium manganate(VII) titrations

Potassium manganate(VII) has the formula $KMnO_4$. It forms a purple solution. Acidified potassium manganate(VII) is an oxidising agent. It reacts with reducing agents such as

- iron(II) ions
- nitrite ions NO_2^-
- sulfite ions SO_3^{2-}

No indicator is required as the solution in the conical flask changes from colourless to pink.

Direct titration

1. Pipette 25.0 cm^3 of the reducing agent eg iron(II) ion solution into a conical flask.
2. Acidify by adding about 15 cm^3 of sulfuric acid (excess) using a measuring cylinder to the conical flask
3. Add standard potassium manganate(VII) solution from the burette into the conical and swirl until the solution changes from **colourless to pink**.

Half equations :

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Combining equations:

$MnO_4^- + 8H+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (×5 to cancel electrons)

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

Overall Ionic Equation:

$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

Note that 1 mol of manganate(VII) ions, MnO_4^-, reacts with 5 moles of iron(II) ions, Fe^{2+}.

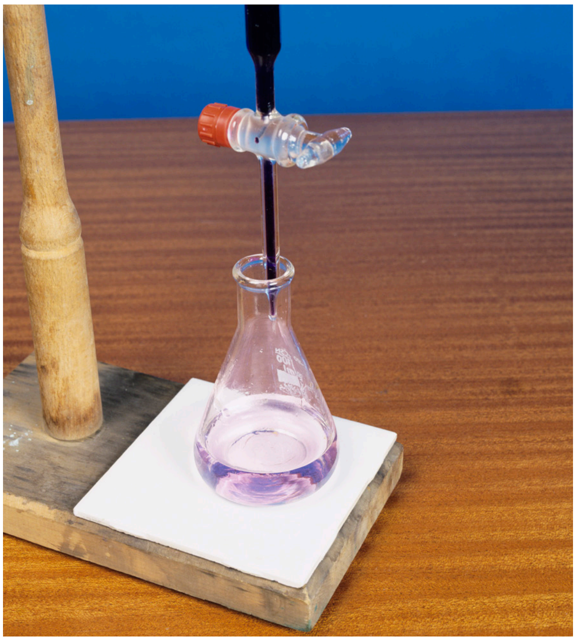
This is a self-indicating titration – there is no need for an indicator.

The purple manganate(VII) solution is decolourised as it reacts with the reductant in the conical, - the first permanent pink colour is the end point – it is caused by the MnO_4 ions as they are no longer being converted to Mn^{2+} because the reductant has been used up.

Titration with iron(II) ions in solution produced from reduction of iron(III) ions

1. A known amount of a reducing agent is added to a known volume of a solution containing iron(III) ions which are in excess. The reducing agent reduces some of the iron(III) to iron(II)
2. Place a known volume (usually 25.0 cm^3) of the reduced solution in a conical flask
3. Acidify the solution with excess dilute sulfuric acid
4. Add standard potassium manganate(VII) solution from the burette into the conical flask and swirl until the solution turns from **colourless to pink.**

At the end point of a potassium manganate(VII)



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and iron(II) ion titration the colour change is from colourless to pink.

This titration is often used to estimate the percentage of iron in iron tablets or the % iron in a solid such as ammonium iron(II) sulfate. FIRST a solution of the tablets/solid is made up.

1. Weigh out x g of iron ammonium iron(II)sulfate/ tablets into a small beaker
2. Add enough deionised water to dissolve the solid and stir with a glass rod
3. Pour into a 250 cm^3 volumetric flask, rinse the glass rod into the beaker, and add all washings to the volumetric flask.
4. Make up the solution to 250 cm^3 by adding distilled water until the bottom of the meniscus is on the mark at eye level.
5. Stopper and invert to mix.

Example : A salt has the formula $Fe(NH_4)_2(SO_4)_2.nH_2O$. The symbol n represents the number of molecules of water of crystallisation.

To find the value of n, 25.0 cm^3 of a solution of ammonium iron(II) sulfate of concentration 31.4 g dm^{-3} were transferred to a conical flask, 10 cm^3 of sulfuric acid were added and the solution then titrated with a solution of potassium manganate(VII) of concentration 0.02 mol dm^{-3}. The results from the titration are shown in the table.

	Rough	Titration 1	Titration 2	Titration 3
Final volume	21.1	20.0	21.6	20.0
Initial volume	0.1	0.0	1.2	0.0
Titre/cm^3	21.0	20.0	20.4	20.0

Calculate the mean titre and justify your answer.

Determine the concentration of the salt solution and use it to find the molar mass of the salt and deduce the value of n.

Answer

First calculate the mean titre – do not use 20.4 as it is not concordant.

$$\text{Mean} = \frac{20.0 + 20.0}{2} = 20.0\ cm^3$$

The equation for the reaction is :

$$5Fe^{2+} + 8H^+ + MnO_4^- \rightarrow 5Fe^{3+} + 4H_2O + Mn^{2+}$$

$$\text{Moles of manganate(VII)} = \frac{20.0 \times 0.02}{1000} = 0.0004\ \text{mol}$$

Ratio is 1 mole manganate(VII): 5 moles Fe^{2+}

5 x 0.0004 = 0.002 mol

Concentration = 0.002 ÷ 40 = 0.08 mol dm^{-3}

$$\text{RFM} = \frac{31.4}{0.08} = 392.5$$

$Fe(NH_4)_2(SO_4)_2.nH_2O = 392.5$

284 + 18n = 392.5

n=6

Back Titration

Back titrations are used for example determine the purity of a Group II metal oxide or carbonate.
A back titration is a method where an excess of a reagent is reacted with a sample. The unreacted reagent is then determined by titration.

To determine the purity of a sample of calcium carbonate the following method may be used.

1. Weigh out a mass of solid eg. calcium carbonate.
2. React it with an excess of acid.

Equation 1: $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$

3. The carbonate is all reacted, but some of the acid (the excess) does not react and is left over. The solution is made up to 250 cm^3 in a volumetric flask.
4. To find how much acid is in excess, titrate a 25 cm^3 portion with standard alkali

Equation 2: $NaOH + HCl \rightarrow NaCl + H_2O$

This allows you to work out the moles of acid in excess - the moles left which did not react with the carbonate.

6. Subtract the excess moles of acid from the moles of acid present at the start and find how much acid reacted with the carbonate. Then use the ratio to find the moles of calcium carbonate, and from this the mass of calcium carbonate present in the sample.

This method can be used to find the pecentage of active ingredient in an indigestion remedy.

Revision Questions

25.0 cm^3 of hydrogen peroxide solution were added to excess acidified potassium iodide solution and the resulting solution made up to 500 cm^3.

25.0 cm^3 of the diluted solution reacted with 36.4 cm^3 of sodium thiosulfate solution of concentration 0.10 mol dm^{-3}.
Which one of the following is the concentration of the undiluted hydrogen peroxide?

A 0.07 mol dm^{-3}
B 0.15 mol dm^{-3}
C 1.46 mol dm^{-3}
D 2.91 mol dm^{-3}

[1]

2 25.0 cm^3 of potassium iodate(V) solution were added to excess potassium iodide solution dissolved in sulfuric acid. The iodine liberated required 30.0 cm^3 of 0.05 mol dm^{-3} $Na_2S_2O_3$ solution. Which of the following is the concentration of the potassium iodate(V) solution?

A 0.01 mol dm^{-3}
B 0.02 mol dm^{-3}
C 0.04 mol dm^{-3}
D 0.05 mol dm^{-3}

[1]

3 Iron(II) oxalate is completely oxidised by acidified potassium manganate(VII). The iron(II) ion is oxidised to iron(III):

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

The oxalate ion is completely oxidised to carbon dioxide.

$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array} \rightarrow 2CO_2 + 2e^-$$

The electrons procuded react with the manganate(VII) ion.

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

(i) Write the equation for the reaction of acidified manganate(VII) ions with iron(II) oxalate.

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[2]

(ii) Oxalic acid is used to remove iron stains because iron dissolves to from iron(II) oxalate. Calculate the mass of iron, in milligrams, dissolved in a 100 cm^3 solution if 20.0 cm^3 of the iron(II) oxalate solution react with 18.2 cm^3 of 0.002 M potassium manganate(VII) solution.

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[4]

Revision Questions

4 A student weighed out 10.0 g of the crushed eggshells and added 100.0 cm^3 of 2.0 mol dm^{-3} hydrochloric acid. The resultant solution was transferred to a 250 cm^3 volumetric flask and made up to the mark with deionised water. 25.0 cm^3 portions of the solution were titrated with 0.10 mol dm^{-3} sodium hydroxide solution. The average titre was found to be 18.0 cm^3.

(i) Calculate the number of moles of sodium hydroxide used in the titration.

.... [1]

(ii) Calculate the number of moles of hydrochloric acid present in the 25.0 cm^3 portion.

.... [1]

(iii) Calculate the number of moles of hydrochloric acid present in the 250 cm^3 volumetric flask.

.... [1]

(iv) Calculate the total number of moles of hydrochloric acid added to the crushed eggshells.

.... [1]

(v) Calculate the number of moles of hydrochloric acid which reacted with the calcium carbonate in the crushed eggshells.

.... [1]

(vi) Calculate the number of moles of calcium carbonate in the crushed eggshells.

.... [1]

(vii) Calculate the mass of calcium carbonate in the crushed eggshells.

.... [1]

(viii) Calculate the percentage, by mass, of calcium carbonate in the crushed eggshells.

.... [1]

Revision Questions

5 Acidified dichromate(VI) ions can be used to determine the concentration of iron(II) ions. The half-equations for the reaction are:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

(i) Write a balanced ionic equation for the reaction between acidified dichromate(VI) ions and iron(II) ions.

.... [1]

(ii) Five iron tablets containing iron(II) sulfate, $FeSO_4$, were dissolved in acid and the solution made up to 250 cm^3 in a volumetric flask. 25.0 cm^3 of this solution required 23.5 cm^3 of 0.01 mol dm^{-3} sodium dichromate(VI) solution for complete oxidation. Calculate the mass of iron(II) sulfate in one iron tablet.

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.... [4]

6 The percentage of calcium carbonate present in egg shells can be found by back titration using excess hydrochloric acid and standard sodium hydroxide solution.

1.12 g of an egg shell were reacted with 20.0 cm^3 of 2M hydrochloric acid and the solution formed made up to 250 cm^3 in a volumetric flask. 25.0 cm^3 of this solution completely reacted with 18.6 cm^3 of 0.1 M sodium hydroxide.

Calculate the percentage of calcium carbonate in the egg shell.

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.... [4]